PATENT SPECIFICATION

(11) 1 396 795

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(21) Application No. 33078/72 (22) Filed 14 July 1972

(23) Complete Specification filed 13 July 1973

(44) Complete Specification published 4 June 1975

(51) INT CL² C23F 7/12

(52) Index at acceptance C7U 4M1 4M2 4Q 7B

(72) Inventors ANTHONY JAMES FERRIE and KEVIN THOMAS McALOON

(19)

(54) COATED METAL

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for providing metals with a corrosion-resistant coating and to metals provided with a corrosion-resistant coating.

According to our invention, copper or alloys thereof, are given a corrosion-resistant coating by a process comprising the steps of

(1) degreasing the metal,

(2) coating the metal with an acidic solution of an aluminium phosphate in at least partly organic solvent the solution containing mineral acid anions and/or carboxylic acid anions in addition to oxyphosphorus acid anions, and

(3) drying the coating and heating the coating at a temperature of at least 50°C.

The first step is conveniently accomplished by solvent treatment, by alkali treatment or by abrasion. It is not essential that the metal is cleaned in the sense of removing oxide and sulphide in this stage because the second stage is effective in cleaning the metal.

Normal aluminium orthophosphate is insoluble in water but soluble in dilute mineral acids (for example hydrochloric and nitric acids) and in some carboxylic acids (for example citric acid) and such solutions containing mineral acid anions and/or carboxylic acid anions in addition to oxyphosphorus acid anions may be used for the purpose of this invention in the second stage of the process. Moreover, solid complex aluminium phosphates containing the anion of the mineral acid and/or carboxylic acid and chemically-bound water or alcohol (or a mixture thereof) may also be used. The complexes containing halogen are described below and in our British Patent Specifications Nos. 1,322,722 and 1,322,724.

The complex phosphates containing anionic groups other than halides are analogous to the halogen-containing complexes and may be prepared and used in analogous ways. Further details of these complexes are given in our co-pending UK Patent Application No. 48576/71 (containing chemically-bound water) (now published as U.K. Patent Specification 1,385,327) and U.K. Patent Specification No. 1,379,561 (containing a chemically-bound organic hydroxy compound especially alcohols).

Referring to the halogen-containing complexes, the halogen is preferably chlorine, but the complexes may contain other halogens, for example bromine.

The solvent used contains an organic solvent and it may consist essentially of an organic solvent, e.g. an alcohol, ester, ketone, aldehyde or ether. Organic solvent molecules may be provided by the use of a complex containing alcohol groups. When aqueous solutions are acquired, addition of an organic co-solvent is needed to operate according to the invention.

Where the complex contains an alcohol group, it is preferred that it is an aliphatic alcohol containing from one to four carbon atoms, for example methyl alcohol, ethyl alcohol, *n*-propyl alcohol or isopropyl alcohol, although complexes with higher alcohols are known and may be used if desired.

The ratio of the number of gram atoms of aluminium to the number of gram atoms of phosphorus in the solution used in the process of the invention may vary over a wide range, for example from 1:3 to 2:1, but is preferably substantially 1:1. The ratio of the number of gram atoms of aluminium to the number of gram atoms of mineral acid anion and/or carboxylic acid anion is preferably substantially 1:1.

The complex halogen-containing aluminium phosphates containing alcohol and their solutions may be prepared by reacting aluminium

or an aluminium compound, preferably a halide, with an alcohol and phosphoric acid.

The complex phosphate containing water can be made as above, or by hydrolysing the alcohol-containing complex phosphates or, for example, by treating aluminium phosphate hydrate with gaseous hydrogen chloride.

After removal of the article to be coated from the coating stage, the final step is accomplished by drying the coating and heating the coating at a temperature of at least 50°C. Temperatures from 50°C to 200°C are preferred although temperatures up to near the melting point of the metal may be used.

Copper and a wide range of its alloys may be processed according to our invention. Bronzes, brasses and related alloys may be used. The metals are given a water and oxygen impermeable coating for use in electrical or decorative applications, or in situations where copper or one of its alloys is associated with a more electronegative metal such as iron or aluminium when the bare metal aids electrochemical corrosion. The coating solution may include conventional corrosion inhibitors such as benzotriazole.

By way of illustration, the results of comparative tests on the protection of copper are given below. Protective coatings of known types and coatings produced according to the process of the invention were applied to copper strips 7.5 cm long and 2.5 cm wide which had been degreased in a trichloroethylene bath. The coated strips were exposed to moist air (90% relative humidity) at a temperature of 46—48°C (cycled over this range). The time to failure (visible tarnishing) is indicated below.

A solution of aluminium chlorophosphate ethanolate (ACPE) containing 8% by weight of the solid material was used to coat similar copper strips, which were also tested. The ACPE was prepared by the method described in Example 1 of U.K. Patent Specification No. 1,322,722 (8% by weight).

Protective Coating	No. of coats	Time to failure (hours)
None	—	2
HCl/ethanol wash	—	0.5
Polyurethane varnish	1	48 discolouration
Polyvinylidene chloride ('Viclan' A85/02) (Registered Trade Mark)	1	5
Benzotriazole 0.25% in water at 60° C	1	20
8% ACPE in methanol heated to 120° C for 30 minutes	1 2	60 160

WHAT WE CLAIM IS:—

1. A process for applying to copper, or an alloy thereof, a corrosion-resistant coating comprising the steps of
   1. degreasing the metal,
   2. coating the metal with an acidic solution of an aluminium phosphate in an at least partly organic solvent the solution containing mineral acid anions and/or carboxylic acid anions in addition to oxyphosphorus acid anions, and
   3. drying the coating and heating the coating at a temperature of at least 50°C.

2. A process according to claim 1 in which the source of aluminium phosphate is a complex aluminium phosphate containing water and/or an alcohol group containing 1 to 4 carbon atoms and a mineral acid anion and/or a carboxylic acid anion in addition to oxyphosphorus acid anion.

3. A process according to claim 1 or claim 2 in which the ratio of gram atoms of aluminium to gram atoms of phosphorus is in the range 1:3 to 2:1.

4. A process according to any one of claims 1 to 3 in which the dried coating is heated at a temperature from 50°C to 200°C.

5. A process as claimed in claim 1 substantially as described and as shown in the Example.

6. Copper or an alloy thereof coated by a process according to any one of claims 1 to 6.

M. JONES,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.